Decomposition of BFRs and emission of dioxins from co-incineration of MSW and electrical and electronic plastics waste

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Introduction

Background
The most common use for BFRs is in building materials, textiles and electronic supplies, e.g. TVs, PCs and photocopiers. In incineration plants with good combustion BFRs will decompose and form other brominated compounds, mainly hydrogen bromide (HBr). In addition, other brominated compounds will also be formed, such as dioxins where chlorine is fully or partly substituted by bromine (brominated and brominated/chlorinated dioxins).

The Norwegian Ministry of the Environment presented in the autumn of 2002 a working plan for reducing the emissions and discharges of BFRs. One action is to investigate the emissions from incineration of waste containing BFRs.

The objective of the project reported in this short paper was to investigate the emissions of dioxin-compounds that may occur from incineration of plastic waste containing brominated flame retardants (BFRs) together with waste from households and the commercial sector. The decomposition of BFRs should also be investigated.

Literature search and initial studies
The objective of the literature search and initial studies was to establish a detailed program for incineration tests at three Norwegian full scale waste incineration plants. It should also be the basis for comparison and evaluation of the results from the measurements.

Investigations in small-scale pilot plants
Incineration tests with waste containing BFRs have been carried out in small-scale pilot plants in Sweden (University of Umeå)[1] and in Germany (TAMARA Plant)[2].

The results from Sweden, where the content of bromine was increased up to 1-2 % by weight, showed that the concentration of halogenated dioxins in untreated flue gas was significantly higher with BFRs than without.
At the TAMARA-Plant, the content of bromine varied from 0 to ca. 0.2 % by weight. Increasing the content of bromine showed no increase in the concentration of chlorinated dioxins, or in brominated or brominated/chlorinated dioxins in untreated flue gas.

Measurements on full-scale plants
Investigations of emissions of brominated dioxins to air were earlier carried out on incineration plants in Denmark, Sweden and Norway. The measurements performed in Denmark[3] also included brominated/chlorinated dioxins. All plants were equipped with advanced flue gas treatment systems. Measurements were performed during incineration of waste from households and the commercial sector (waste with low BFR content), and results showed very low levels for all analysed dioxins.

Emission measurements have been carried out at a Japanese incineration plant burning plastic waste containing BFRs, mixed with waste from households and the commercial sector[4]. Total input of BFRs was less than 500 g/hr, and the emission to air of PBDE (polybrominated diphenyl ethers) and TBBPA (tetrabrombisphenol) was respectively 3.5 and 8 ng/Nm^3.

Incineration tests at three Norwegian plants
The main goal of the incineration tests was to establish the flue gas concentration of brominated, chlorinated and brominated/chlorinated dioxins before and after flue gas cleaning, and with different proportions of plastic waste containing BFRs. To verify the input, the contents of bromine and chlorine in all output flows (bottom ash, fly ash, scrubber water and flue gas) were analysed. The decomposition of BFRs was investigated by analysing BFRs in output flows.

Methods and materials

The incineration test included sampling and analysis at two larger plants for mixed municipal waste, and one smaller plant for shredded industrial waste. The brominated waste added was waste from a plant for demolition of electric and electronic devices. It was estimated to contain approximately 1 % by weight bromine. Approximately 80% of this contained PBDE.

The most extensive measurements were performed at the largest municipal waste incineration plant in Oslo (Klemetsrud Plant, capacity 155.000 tons of waste per year). The plant has two incinerator lines, each with the capacity of incinerating 10 tons of waste per hour. Each line is equipped with a flue gas cleaning system, consisting of a bag house filter with active coal injection, and a wet scrubber.

At this plant sampling and analysis were carried out in three different situations:
- No addition of brominated waste
- Mix with 5 % by weight brominated waste; i.e. ca. 0.05 % by weight bromine in total waste.
- Mix with 10 % by -weight brominated waste; i.e. ca. 0.1 % by weight bromine in total waste.

At the second plant (FREVAR Plant, Fredrikstad, capacity 155 000 tons of waste per year) measurements were carried out with no addition of BFRs.

At the third and smaller plant (Energos Plant, Ranheim, capacity 10 000 tons of waste per year) measurements were performed incinerating a mix with 0 and 20 % by weight bromine containing waste (i.e. 0.2 % by weight bromine in the total mix).

Outputs from the plant in Oslo were sampled and analysed. These outputs are the bottom ash (BFR, total chlorine and bromine), fly ash (BFR, total chlorine and bromine) emission to air (BFR and dioxins), and scrubber water (BFR and total chlorine and bromine). In addition flue gas before cleaning was sampled and analysed (total gaseous chlorine and bromine and dioxins). Some samples were taken only with the highest concentration of BFR in the waste. Emission to air (BFR and dioxins), the bottom ash (BFR, dioxins and total chlorine and bromine) and flue gas samples before cleaning (total chlorine and bromine) were sampled and analysed at the Energos Plant. Measurements of Emission to air (BFR and dioxins) and the flue gas before cleaning (gaseous chlorine and bromine) were sampled at FREVAR.

Necessary measurements of concentration of oxygen, temperature, humidity and mass flow were performed in addition.

The BFR analysed were Tribromanisol (TBA), PBB-15, 49, 52, 153, PBDE-28, 47, 71, 77 99, 100, 119, 138, 153, 154,183, 209, Tetrabrombisfenol-A (TBBPA) and α-, β-, γ-Hexachlorcyclo-dodekan (HBCD). The dioxins analysed included at least 17 chlorinated dioxins/furans, groups of brominated and combined chlorinated/brominated dioxins/furans.
Methods for sampling and analysis are mainly based on European standards. Emission to air and in flue gas upstream of the bag filter were sampled and analysed according to European standards, EN 1948-1, -2 and –3 by the cooled probe method. C13-labeled standards were added in the field. Emission of gaseous chlorine and bromine were analysed according to EPA Meth.26A. The numbers of samples for each parameter at each plant and situation were 2-3 samples for BFR and dioxins and 3-4 samples for gaseous chlorine and bromine.

Several sub samples of bottom ash and fly ash were taken during the day when the test were carried out. These samples were mixed, homogenised and divided before 1-2 laboratory samples were analysed.

Results and discussion

The incinerating conditions during sampling and measurements at Klemetsrud Plant (Oslo) were normal for the plant, with average CO-levels at ca. 20-30 mg/Nm^3. During sampling at the FREVAR Plant average CO-levels were ca. 50 mg/Nm^3. At FREVAR Plant they also experienced some problems with the fabric filters during the measurements.

At the Energos Plant (Ranheim) CO was not detectable, which indicates that incineration was good.

Bromine in output flows

Measured results for gaseous bromine in untreated flue gas during incineration of normal waste mix indicates a bromine content equal to or lower than what is common for waste from households and the commercial sector.
Measured results of bromine in output flows at Klemetsrud Plant (Oslo) and at the Energos Plant (Ranheim) indicate that the content of bromine in the plastic mixture was correctly estimated.

Brominated flame retardants (BFRs)
The amount of BFRs in the waste mixture used in the tests at Klemetsrud Plant (Oslo) was not analysed, but calculated/estimated to be ca. 30 kg/hr. The measured results confirm that BFRs decompose in the incineration process. The amount of BFRs in output flows is less than 0.001 % by weight of the total amount of BFRs in the waste mix (see figure 1 below).

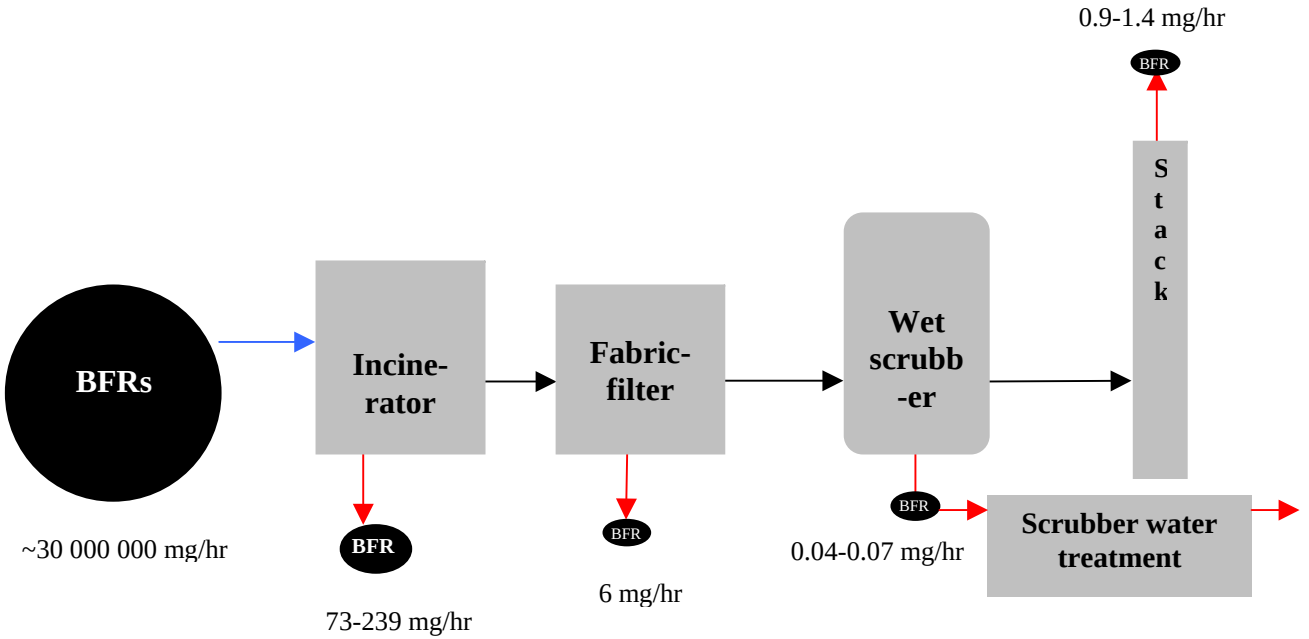

Figure 1: *Observed input and output flows of brominated flame retardants at Klemetsrud Plant (Oslo) with 10 % by weight addition of brominated waste.*

The concentration of BFRs in flue gas from Klemetsrud Plant (Oslo) was 14-22 ng/Nm^3. This equals 0.9-1.4 mg/hour and ca. 0.01 kg/year, assuming 8000 running hours/year at the same emission level. A Danish investigation[5] estimates the total national Danish emissions of BFRs from incineration to be < 0.04 tons. A report from the Norwegian National State Pollution Control Authority (SFT)[6], estimates the national emissions from combustion in Norway to be < 0.01 tons (1998), i.e. < 10 kg/year.

At the Energos Plant (Ranheim) the reported concentration of BFRs in the flue gas was <5 ng/Nm^3.

The concentration of BFRs in bottom ash from the tests at Klemetsrud Plant (Oslo) shows levels far below the threshold value stated in the Norwegian regulations for Hazardous waste.

DekaBDE and TBBPA (Tetrabrombisphenol A) are the dominating compounds of BFRs in the bottom ash at Klemetsrud Plant (Oslo). In the flue gas dekaBDE has the highest concentration level.

Concentration of dioxins in emissions to air (after cleaning)
Figure 2 shows emissions of chlorinated, brominated and chlorinated/brominated dioxins without any addition of brominated waste, and with the addition of 5 % by weight, 10 % by weight and 20 % by weight bromine containing waste. (The results are reported as actual emission , not toxic equivalents).

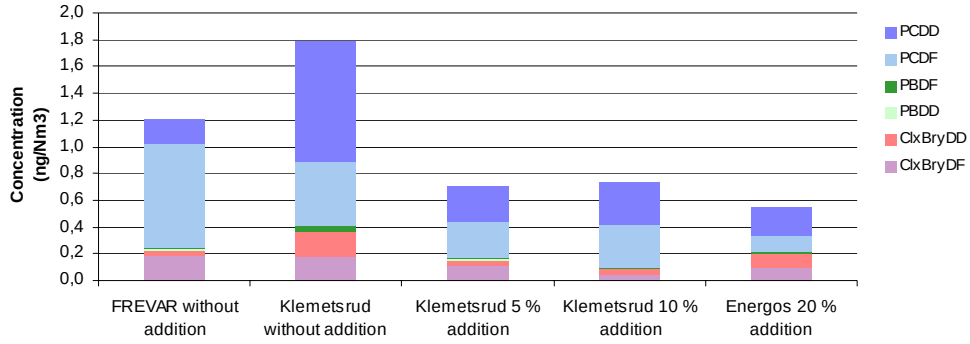

Figure 2: *Emissions of chlorinated, brominated and chlorinated/brominated dioxins. The results are reported as actual emission, not toxic equivalents.*

Emissions of chlorinated dioxins (PCDDs/Fs), in terms of Nordic toxic equivalents, resulting from the addition of brominated waste, are presented in the figure 3.

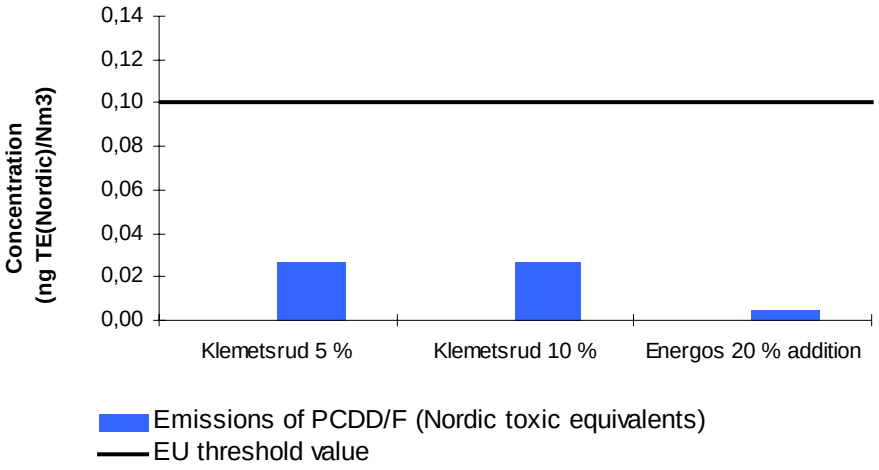

Figure 3: *Emissions of chlorinated dioxins (PCDDs/Fs), in terms of Nordic toxic equivalents, resulting from addition of brominated waste.*

Uncertainty in sampling and analysis, variations in operating conditions and waste mixture, differences between laboratories with respect to methods of analysis (especially dioxins), makes comparison of results difficult. We may although draw the following main conclusions:

- Increasing the content of BFRs in the waste gave no significant increase in the emissions of chlorinated dioxins, or either brominated and chlorinated/brominated dioxins
- The emission level is highest for chlorinated dioxins, lower for chlorinated/brominated dioxins and lowest for brominated dioxins
- The emission levels for chlorinated dioxins, reported as Nordic toxic equivalents, are low compared to emission threshold value in the EU-directive for incineration of waste. The reported emission levels were 0.03 ng/Nm^3 and 0.006 ng/Nm^3 respectively for the Klemetsrud Plant (Oslo) and Energos Plant (Ranheim), and the EU threshold value is 0.1 ng/Nm^3.
- The emission measurement results indicate that the incineration efficiency and the operating conditions of the flue gas treatment systems are of greater importance to the resulting emission levels for dioxins, than the bromine content level.

Concentration of dioxins in emissions before and after flue gas cleaning

Measurements of dioxins in the flue gas before and after flue gas cleaning were carried out with addition of 10 % by weight bromine containing waste at the Klemetsrud Plant (Oslo)

The concentration of chlorinated/brominated dioxins before cleaning was ca. 28 ng/Nm^3, which was three times the concentration of chlorinated dioxins. After cleaning the concentration was ca. 0.1 ng/Nm^3. This gives a removal efficiency for chlorinated/brominated dioxins of >99% and for chlorinated dioxins ca. 93%. The removed dioxins end up in the fly ash from the fabric filter, which is treated as hazardous waste. See figure 4.

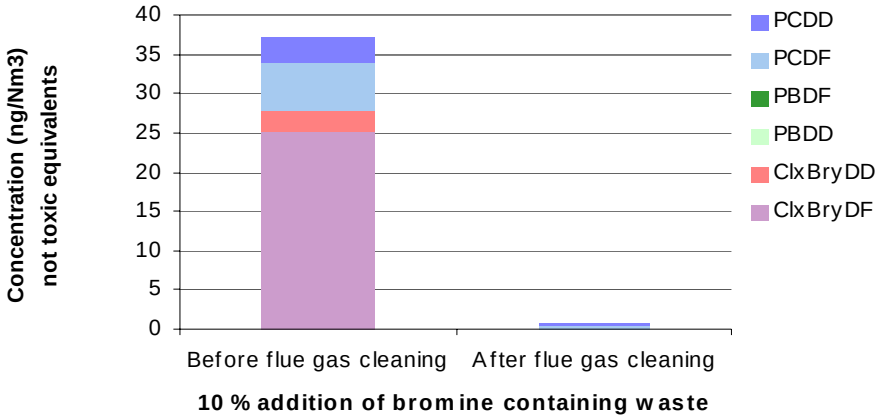

Figure 4: *Concentration of chlorinated, brominated and chlorinated/brominated dioxins in flue gas before and after flue gas cleaning, Klemetsrud Plant (Oslo). The levels are given as actual measured levels, not corrected for toxicity equivalents.*

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